

## CHEMICALLY CONTROLLED MORPHOLOGY OF ZEOLITE A CRYSTALS

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### INTRODUCTION

Although most of applications of zeolites are closely related to their structural and chemical properties (i.e., type of zeolite, modification by ion exchange and/or isomorphous substitution etc.), size and shape of zeolite crystals may play a crucial role in the mode and efficiency of their application [1,2]. Due to unique applications of zeolite A as absorbents, ion-exchangers and especially detergent builders [1,2], many attempts were focused on the investigations of various factors which control the crystallization pathway and particulate properties of the crystalline end product (zeolite A). While alkalinity of reaction mixture has the most expressive effect on the crystal size [3,4], crystal habit of zeolite A can be modified by the aluminum content (or better to say by the batch molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) in the reaction mixture [3,5]. Basaldella *et al.* [3] have found that zeolite A having perfect cubic crystals with sharp edges and apexes, are obtained when  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is in the range from 2.69 to 2.4, the crystals with truncated edges and apexes, are obtained in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  range from 1.48 to 1.99, and a mixture of both the morphological features are obtained in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  from 2.18 to 2.41. In a more detail study, Thompson and Huber [5] have found that a decrease of the batch molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  from 1.5 to 0.975 increases the edge-to-face aspect ratio from 0 (perfect cubic crystals with sharp edges and apexes) to 0.2 (the crystals with truncated edges and apexes). This implies that further decrease of the batch molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (below 0.975) would increase the edge-to-face aspect ratio above 0.2, and thus result in possibly bi-pyramidal or even poly-hedral zeolite A crystals. In addition, knowing that increase of concentration of reactive silicate, aluminate and aluminosilicate ions in the liquid phase, caused by increase of alkalinity [6], induces intense surface nucleation and “rounding” of edges and apexes of zeolite A crystals [7], one can assume that even rounded-shape particles of zeolite A can be obtained at low value of the batch molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  combined with relatively high alkalinity of reaction mixture. To check these theses, zeolite A was synthesized in wide ranges of the chemical parameters ( $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2/\text{H}_2\text{O}$  and  $\text{Na}_2\text{O}/\text{H}_2\text{O}$ ) which determine the chemical composition of the reaction mixture (hydrogel).

### EXPERIMENTAL

Aluminosilicate hydrogels having the batch molar compositions:  $x\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$  in a wide range of the batch molar ratios  $x = [\text{Na}_2\text{O}/\text{H}_2\text{O}]_b$ ,  $y = [\text{SiO}_2/\text{Al}_2\text{O}_3]_b$  and  $y/z = [\text{SiO}_2/\text{H}_2\text{O}]_b$  were prepared at ambient (room) temperature by rapid pouring of sodium silicate solution having appropriate concentrations with respect to  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  into a plastic beaker contained vigorously stirred (by propeller) sodium aluminate solution having appropriate concentrations with respect to  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ .

The aluminosilicate hydrogels, prepared as described above are transferred into stainless-steel reaction vessel preheated at crystallization temperature (80 °C) and heated at

crystallization temperature under stirring with a Teflon-coated magnetic bar driven by magnetic stirrer, until the entire amount of the amorphous aluminosilicate (gel) is transformed into zeolite. The product (zeolite) was separated from the liquid phase (supernatant) by centrifugation, washed with demineralised water and dried overnight at 105 °C.

X-ray diffraction patterns of the samples were taken by a Philips PW 1820 diffractometer with vertical goniometer and  $\text{CuK}\alpha$  graphite radiation in the corresponding region of Bragg's angles ( $2\theta = 5 - 50^\circ$ ).

Shape of zeolite particles (crystals) was determined from SEM photographs of appropriate samples. The SEM photographs were taken by Philips XL 30, scanning-electron microscope.

Particles (crystals) size distribution curves of the crystalline end products (zeolite A) are determined with a Malvern Mastersizer 2000 laser light-scattering particle size analyzer.

Real specific surface area of powdered samples,  $RSSA$ , was determined by multiple BET method (Gemini 2360 Surface Area Analyzer, Micromeritics) using nitrogen as adsorbate at the temperature of liquid nitrogen (-195.6 °C).

Average crystal size  $L_{av}$ , specific number of crystals,  $N_s$  and geometrical specific surface area,  $GSSA$  were determined/calculated from the corresponding crystal size distribution data, using the appropriate calculation procedures [8].

## RESULTS AND DISCUSSION

Hydrothermal treatment of hydrogels in wide range of chemical composition defined by the batch molar ratios  $x = [\text{Na}_2\text{O}/\text{H}_2\text{O}]_b$ ,  $y = [\text{SiO}_2/\text{Al}_2\text{O}_3]_b$  and  $y/z = [\text{SiO}_2/\text{H}_2\text{O}]_b$  resulted in formation of at least four morphological entities of zeolite A; three of them, namely (i) regular cubic crystals with “sharp” edges (Fig. 1a), (ii) cubic crystals with truncated edges (Figs. 1b and 1c) and (iii) cubic crystals with “rounded” edges (Fig. 1d) are well known as “standard” morphological features of zeolite A [2-5,7]. Generally, regular cubic crystals with “sharp” edges can be obtained when  $x \leq 0.0136$ ,  $y/z \leq 0.0026$  and  $2 \leq y \leq 2.2$  cubic crystals with truncated edges can be obtained when  $0.0051 \leq x \leq 0.037$ ,  $0.0026 \leq y/z \leq 0.0162$  and  $y < 2$  (these conditions are close to those reported by Basaldella *et al.* [3]) and cubic crystals with “rounded” edges and apexes can be obtained when  $x \geq 0.037$  and  $y \leq 1.4$ .

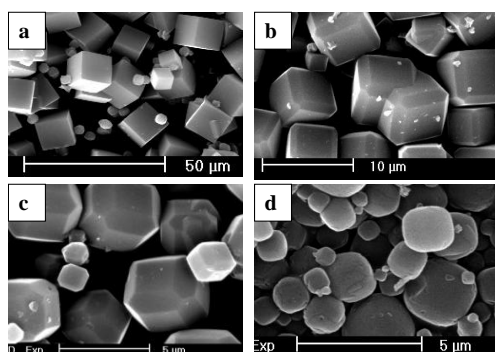


Figure 1. “Standard” morphological features of zeolite A: (a) regular cubic crystals with “sharp” edges and apexes; (b) cubic crystals with truncated edges and apexes having the aspect ratio  $w_e/L = 0.12$ ; (c) cubic crystals with truncated edges and apexes having the aspect ratio  $w_e/L = 0.2$ ) and (d) cubic crystals with “rounded” edges and apexes.

Further increase of alkalinity and simultaneous decrease of the batch molar ratio  $y = [\text{SiO}_2/\text{Al}_2\text{O}_3]_b$  causes a complete loss of crystal faces, and thus appearing pseudo-spherical, face-less particles of zeolite A for  $0.037 \leq x \leq 0.042$ ,  $1.2 \leq y \leq 1.4$  and  $0.018 \leq y/z \leq 0.032$ . Fig. 2 shows that this morphological form of zeolite (internally named **Face-Less zeolite A**; abbreviated - zeolite FLA) appears in the form of discrete pseudospherical particles (Fig. 2a) with rough external surfaces (see Fig. 2b) and the size in the range from 0.5  $\mu\text{m}$  to 4  $\mu\text{m}$ .

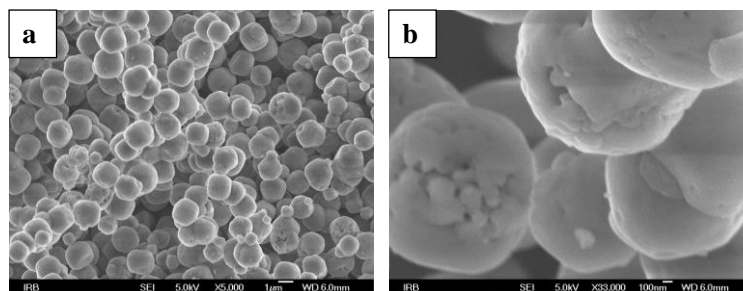


Figure 2. SEM photograph of face-less zeolite 4A particles magnified for 10000 times (a) and for 33000 times (b)

The specific sight of the surface of FLA particles leads to reasonable deliberation that specific surface area of FLA, and thus its absorption ability is not the function of only particle size [9] and specific interaction between absorbents (zeolite A) and absorbate (e.g., electrically neutral molecules), but also of the surface roughness of FLA particles. Or in the other words, it is certain that for the same particle size the absorption ability of FLA is considerably higher than the absorption ability of “standard” zeolite A represented by morphologies shown in Figs. 1a – 1d. To determine in which extent the absorption ability of FLA is higher than the absorption ability of the “standard” zeolite A, both the real (BET), *RSSA*, and geometrical, *GSSA*, specific surface area of the samples  $S_{\text{SEA}}$  (zeolite A having regular cubic crystals with “sharp” edges and apexes, Fig. 1a),  $S_{\text{TEA-1}}$  (zeolite A having cubic crystals with truncated edges and apexes;  $e/L = 0.14$ , Fig. 1b),  $S_{\text{TEA-2}}$  (zeolite A having cubic crystals with truncated edges and apexes;  $e/L = 0.22$ , Fig. 1c),  $S_{\text{REA}}$  (zeolite A having crystals with rounded edges and apexes, see Fig. 1d) and  $S_{\text{FLA}}$  (zeolite FLA; Fig.2) were measured/calculated and analyzed.

Table 1. Average crystal size,  $L_{\text{av}}$ , specific number of crystals (number of crystals in 1 g of the sample),  $N_s$ , geometrical specific surface area, *GSSA*, real specific surface area, *RSSA* and the ratio *RSSA/GSSA* of the samples  $S_{\text{SEA}}$ ,  $S_{\text{TEA-1}}$ ,  $S_{\text{TEA-2}}$ ,  $S_{\text{REA}}$  and  $S_{\text{FLA}}$ .

Sample	$L_{\text{av}}$ ( $\mu\text{m}$ )	$N_s$ (#/g)	<i>GSSA</i> ( $\text{m}^2/\text{g}$ )	<i>RSSA</i> ( $\text{m}^2/\text{g}$ )	<i>RSSA/GSSA</i>
$S_{\text{SEA}}$	1.662	$9.672 \times 10^{10}$	1.630	$1.4724 \pm 0.022$	0.908
$S_{\text{TEA-1}}$	1.303	$6.650 \times 10^{10}$	0.908	$0.9410 \pm 0.009$	1.036
$S_{\text{TEA-2}}$	1.583	$1.233 \times 10^{11}$	1.446	$1.5060 \pm 0.0273$	1.041
$S_{\text{REA}}$	1.291	$5.880 \times 10^{10}$	0.939	$1.0920 \pm 0.0144$	1.163
$S_{\text{FLA}}$	1.237	$2.673 \times 10^{11}$	1.593	$4.4331 \pm 0.061$	2.783

The data in Table 1 and Figs. 1 and 2 undoubtedly show that regardless to the differences in the particulate properties ( $L_{av}$ ,  $N_s$ ,  $GSSA$  and  $RSSA$ , crystal shape), the value of  $RSSA/GSSA$  is approximately constant and close to 1 for the “standard” zeolite A represented by the samples  $S_{SEA}$ ,  $S_{TEA-1}$ ,  $S_{TEA-2}$  and  $S_{REA}$ . On the other hand, since the  $GSSA$  value of the sample  $S_{FLA}$  is comparable with the  $GSSA$  values of the samples  $S_{SEA}$ ,  $S_{TEA-1}$ ,  $S_{TEA-2}$  and  $S_{REA}$  [ $GSSA(FLA)/GSSA(\text{“standard”}) = 0.977 - 1.75$ ] and at the same time, since the  $RSSA$  value of the sample  $S_{FLA}$  is considerably higher than the  $RSSA$  values of the samples  $S_{SEA}$ ,  $S_{TEA-1}$ ,  $S_{TEA-2}$  and  $S_{REA}$  [ $RSSA(FLA)/RSSA(\text{“standard”}) = 2.94 - 4.71$ ], the real specific surface ratio of zeolite FLA (sample  $S_{FLA}$ ) is about 2.8 times higher than its geometrical specific surface ratio, and thus that the ratio  $RSSA/GSSA$  of zeolite FLA is 2.4 – 2.8 times higher than the  $RSSA/GSSA$  ratio of the “standard” zeolite A. Or in the other words, the absorption ability of zeolite FLA is 2.4 – 2.8 times higher than the absorption ability of the “standard” zeolite A having the same crystal size distribution as zeolite FLA.

## CONCLUSION

Although there is not a reasonable theory which strictly explains the influence of the ratio  $y = [SiO_2/Al_2O_3]_b$  on morphological properties of zeolite A, it is evident that that decrease of  $y$  ( $y \leq 2$ ) at relatively high alkalinity (e.g.,  $x > 0.005$ ) decreases the crystal growth rate in  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions, and thus development of  $\{110\}$  and  $\{111\}$  crystal faces (see Figs. 1b and 1c). Also is evident that further increase of alkalinity and simultaneous decrease of  $y$  causes surface nucleation and “rounding” of crystal edges and apexes [7] for  $x \geq 0.037$  and  $y \leq 1.4$  (see Fig. 1d) and that for  $0.037 \leq x \leq 0.042$ ,  $1.2 \leq y \leq 1.4$  and  $0.018 \leq y/z \leq 0.032$  the growth rate is approximately same in all directions, which causes the disappearing of individual crystal faces and formation of pseudospherical particles of zeolite FLA (see Fig. 2). The high roughness of the particle surfaces (see Fig. 2b) indicates that intense surface nucleation [7] and rapid “uncontrolled” growth of the formed surface nuclei occurs under relatively high alkalinity of system ( $0.037 \leq x \leq 0.042$ ). This high surface roughness is the reason that the absorption ability of unit external geometrical surface area (e.g.,  $1 \text{ m}^2$ ) of zeolite FLA is about 2.4 – 2.8 times higher than the absorption ability of the unit geometrical surface area of “standard” zeolite 4A.

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